

# THE INSOLUBLE RESIDUE TEST FOR ABUNDANCE OF CARBONATE

J. GRAHAM COGLEY\* AND M. AIKMAN

*Department of Geography, Trent University, Peterborough, Ontario, Canada K9J 7B8*

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## ABSTRACT

Among methods for determining the abundance of carbonate minerals in solid samples, dissolution in acid is appealing because it is cheap and can be quick, but it suffers from several sources of uncertainty. The weight loss due to evaporation of water can be corrected for easily by measuring the weight loss from blank vessels as well as sample vessels. However, a further correction, for excess evaporation due to heat liberated by dissolution, is desirable; we show how to calculate it. Certain puzzling results point to a need for further investigation of interfering factors. © 1997 John Wiley & Sons, Ltd.

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KEY WORDS: insoluble residue; carbonate abundance; laboratory techniques

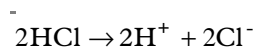
## INTRODUCTION

While investigating the provenance of glacial sediments in central Ontario (Cogley *et al.*, 1997) we needed to make a substantial number of rapid, inexpensive measurements of carbonate abundance in samples of till. We chose the insoluble residue test, which involves digesting the sample in acid and equating weight loss during digestion with loss of carbon dioxide gas. It became clear during development of a protocol that careful control of uncertainties was warranted. In particular, correction for evaporation of water is essential if the method is to be better than semiquantitative. A further correction, for excess evaporation due to the heat released by dissolution, is also desirable and is not difficult to apply.

This simple method may thus merit renewed attention from those who need to estimate carbonate abundance in solid samples. A number of variations of the method have been proposed in the past; several are discussed by Goh *et al.* (1993), and the procedure of Dreimanis (1962) remains in use. Dreimanis's Chittick apparatus is designed to give a careful volumetric accounting of the gas evolved during digestion, and his evaporative temperature correction rests on the same principle as ours. However, our protocol is much simpler. It requires only ordinary laboratory supplies, an accurate balance and hydrochloric acid, and it offers rapid throughput. Making good use of a stopwatch, one worker can readily process a blank and five samples – all consisting of three replicates – in less than one hour.

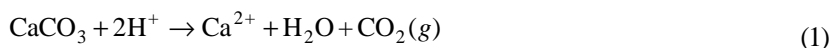
## BASIS OF THE METHOD

When calcite or related carbonates react with an excess of hydrochloric acid, calcium ion is expected to go into solution while the carbonate is driven off as carbon dioxide gas:



\* Correspondence to: J. G. Cogley

followed by



Note that any  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  ions produced as intermediates will themselves react with  $\text{H}^+$  when the latter is present in excess. Thus, if other causes of weight loss can be corrected for, Reaction 1 offers a means of reconstructing the original abundance of  $\text{CaCO}_3$ : multiplying corrected weight loss by  $M_c = 100.09/44.01 = 2.274$ , the ratio of molecular weights of  $\text{CaCO}_3$  and  $\text{CO}_2$ , gives the original weight of calcite. The other major causes of weight loss are likely to be evaporation of water and dissolution of carbonate minerals other than calcite.

The essence of the method is that carbonate minerals are the only ones which will yield a gaseous dissolution product. In their variant method, Shilts and Kettles (1990) weighed the dried solid residue after digestion and concluded that the results were unreliable because other minerals besides the carbonates, notably some phyllosilicates, react with  $\text{HCl}$ ; some non-carbonate species were lost when the expected (and highly soluble)  $\text{CaCl}_2$  precipitate was washed out of the solid residue before drying.

## EXPERIMENTAL METHODS

We collected 112 samples, each consisting of three separate subsamples from within 1–2 m of each other, at suitable localities where till was exposed without vegetation cover or visible soil-profile development. The sand (2.0–0.062 mm) was separated from coarser grains in the field, and from finer sediment in the laboratory after drying.

Many of the carbonate measurements had to be repeated after we discovered an error in our original guide to procedure (Briggs, 1977). This source stipulates using 20 ml of 2 M  $\text{HCl}$  to digest 5–10 g of dry sample, a ratio which left some of our samples still effervescent when more acid was added after substantial digestion times. Reaction 1 shows, however, that 20 ml of 2 M acid (0.04 mol) can digest only 0.02 mol, or 2 g, of  $\text{CaCO}_3$ .

We therefore prepared subsample aliquots of 3–4 g by repeated quartering, weighed each aliquot to 0.1 mg and digested it in an excess (40 ml) of 2 M  $\text{HCl}$ . Beakers containing acid were kept covered (with the aliquot containers) until the aliquots were added to them, and digestion was allowed to proceed for 30 min. To stop sample material or acid escaping by effervescence, beakers of 600 ml capacity were chosen. On the assumption that all carbonate is calcite (see below), the fractional carbonate abundance was calculated as:

$$c = M_c f(w_t - w_b) / W_s \quad (2)$$

where  $w_t$  is the measured weight loss from the sample beaker,  $w_b$  a 'blank' correction,  $W_s$  the original weight of the aliquot of sand, and  $f$  a correction factor (explained below).

Evaporative loss of  $\text{H}_2\text{O}$  was corrected by subtracting the average weight loss  $w_b$  of several blank beakers, containing 40 ml 2 M  $\text{HCl}$  but no sand, from the weight loss of each sample. Blank and sample beakers, of the same capacity, were kept side by side on an ordinary laboratory bench. Ways of trapping vapour with special apparatus are available (Goh *et al.*, 1993) but, with a possible exception noted later, we found that the simple blank correction to measurements on freely evaporating samples was entirely satisfactory.

Estimates of carbonate abundance would be too high by 8–9 per cent if all the carbonate were dolomite and not calcite. Chapman and Dell (1963) report that calcite is several to many times more abundant than dolomite in the Palaeozoic limestone formations underlying our study till. Therefore we do not correct for dolomite, and we further assume that magnesite and siderite are absent.

Table I. Weight loss rates ( $\text{mg min}^{-1}$ ) during measurements of digestion

Interval (min)	E1	E2	E3	E4	E5	Blank
0–7	133.3 $\pm$ 3.2	105.4 $\pm$ 5.0	24.2 $\pm$ 3.6	–9.6 $\pm$ 1.5	–9.7 $\pm$ 1.5	27.2 $\pm$ 1.2
7–15	10.5 $\pm$ 2.0	13.6 $\pm$ 1.9	8.3 $\pm$ 1.9	–2.8 $\pm$ 0.7	–3.2 $\pm$ 0.7	10.5 $\pm$ 0.5
15–23	2.0 $\pm$ 0.6	4.1 $\pm$ 0.3	2.0 $\pm$ 1.3	–2.7 $\pm$ 0.5	–3.3 $\pm$ 0.3	11.3 $\pm$ 0.3
23–32	2.9 $\pm$ 1.0	2.4 $\pm$ 0.7	0.2 $\pm$ 1.4	–2.9 $\pm$ 0.5	–3.7 $\pm$ 0.5	10.2 $\pm$ 0.3
32–60	0.2 $\pm$ 1.0	0.3 $\pm$ 1.0	–2.1 $\pm$ 0.8	–3.7 $\pm$ 0.8	–4.2 $\pm$ 0.6	11.1 $\pm$ 0.6
60–121	–0.1 $\pm$ 1.3	–1.4 $\pm$ 1.0	–2.5 $\pm$ 0.9	–4.1 $\pm$ 1.2	–4.9 $\pm$ 0.8	10.4 $\pm$ 0.8

For the samples E1–E5 the figures are corrected estimates of weight loss rate: average evaporation rate from blank beakers (far-right column) has been subtracted from average weight loss rate of the sample beakers. Negative loss rates do not imply a gain of weight but rather a procedural problem (see text). Sample loss rates averaged over three, and blank rates over five, replicate beakers. Error range given is twice the standard error.

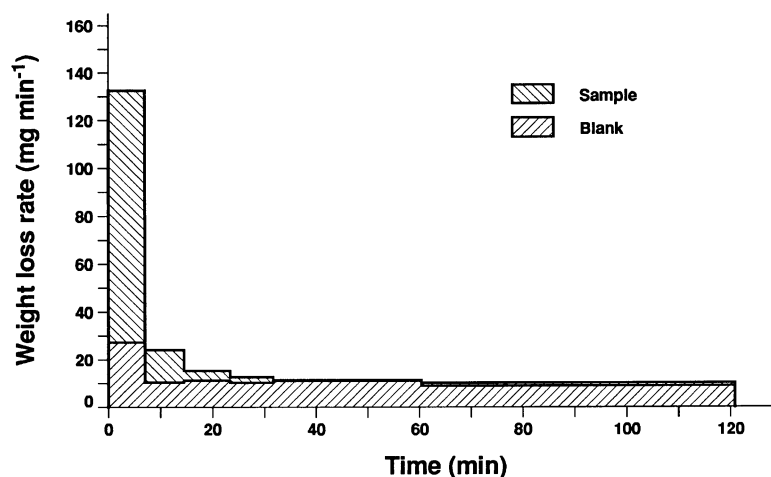


Figure 1. Total weight loss rate from a typical sample (E2, see Table I) of till-derived sand during digestion by 2 M HCl, and evaporation rate from a blank containing 2 M HCl but no sand. The weight loss rate decreases exponentially, as expected; after 30 min all of the loss is due to evaporation

## RESULTS

### Digestion time

On the basis of exploratory tests (Table I, Figure 1) we concluded that a standard digestion time of 30 min was a reasonable compromise which would ensure complete or nearly complete digestion of calcite without evaporation becoming proportionately large (for moderately and highly soluble samples). Reproducibility, as measured by the standard error, was generally good (Table I). However, the additional uncertainty in smaller estimates of  $c$ , because the blank correction is proportionately large when the total weight loss is small, requires careful tracking of errors. Usually the uncertainty in the blank correction is the largest component of the total uncertainty, but failure to make the correction would be a substantially more serious error.

We do not have a convincing explanation for why two samples (E4 and E5) have evaporation rates significantly less than the blank. Nor can we explain why the blank-beaker evaporation rate decreased during the early part of the test illustrated in Figure 1. These puzzles are discussed further below.

### Excess evaporation due to heating

Reaction 1 releases heat. Although the heat balance of the sample system (sand, acid and water, beaker, evolving gas and superjacent air) is actually quite complicated, there will certainly be more evaporation from the hotter sample beaker, proportional to the temperature-dependent difference in saturation vapour pressure, and the blank correction will be too small.

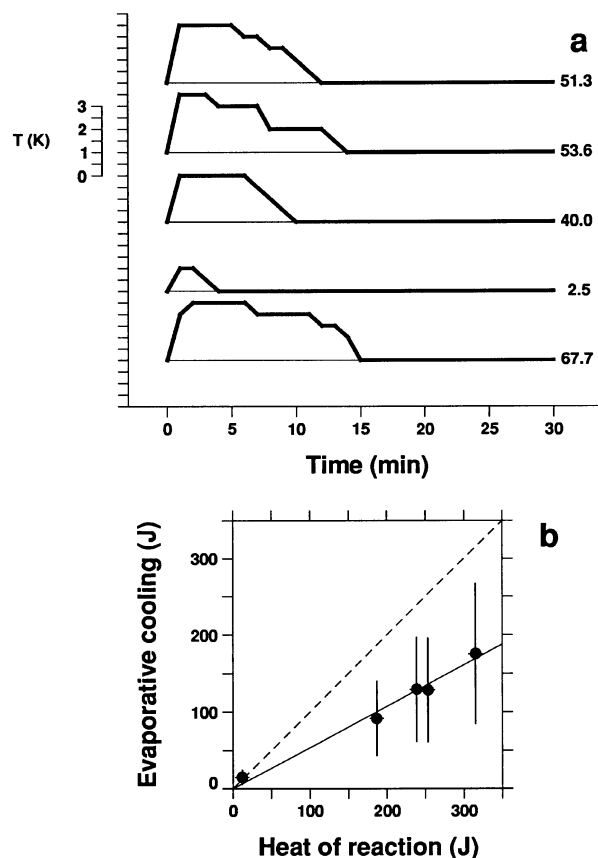


Figure 2. (a) The evolution of excess temperature (above the temperature of a blank beaker of acid) during five digestion measurements. Time series are offset from each other by 3 K for clarity. The percentage abundance of CaCO<sub>3</sub> digested is shown for each measurement at the right (from Equation 2 with  $f=1$ ). (b) An interpretation of the rough correspondence observed in (a) between the area under each curve and the amount of CaCO<sub>3</sub> digested. The heat released by Reaction 1, and the (extra) latent heat dissipated by evaporation at the elevated temperatures shown in (a), are calculated as described in the text. Dashed line: a hypothetical system in which evaporation dissipates all of the heat of reaction. Solid line: ratio of calculated heat of reaction to calculated evaporative cooling; this line has a slope of  $53 \pm 12$  per cent.

We can estimate the heating, and therefore the excess evaporation. The enthalpy change  $\Delta H$  for Reaction 1 follows from the molar enthalpies of formation of the participating species in their standard states (e.g. Atkins, 1994). It is a decrease,  $\Delta H = -0.153 \text{ J mg}^{-1}$  of digested CaCO<sub>3</sub>. If all of this energy were used to heat the  $\sim 37 \text{ g}$  of H<sub>2</sub>O in the system (with a specific heat capacity of  $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ ) the water temperature would rise by  $0.99 \text{ K g}^{-1}$  of digested CaCO<sub>3</sub>.

Using ordinary thermometers, we measured temperature to the nearest 0.5 K at 1-min intervals in several paired blank and sample beakers. The sample temperature excess (Figure 2a) over the blank beaker (consistently at 296 K) was non-zero for up to 15 min following the start of digestion. The integral of the temperature excess over time appears to be roughly proportional to the estimated carbonate abundance as given at the right of each curve. This is not a coincidence.

Assuming that the system is at a uniform temperature  $T$ , the blank correction may be expressed as:

$$\begin{aligned}
 w_b &= \gamma \int_0^t [e_*(T) - e_a] dt' \\
 &= \gamma \int_0^t (1-r)e_*(T) dt'
 \end{aligned}
 \tag{3}$$

where  $t$  is the duration of the measurement (min),  $e_*(T)$  is the saturation vapour pressure (Pa),  $e_a = r e_*(T)$  is the vapour pressure of the air in contact with the beaker contents (Pa),  $r$  is the relative humidity, and  $\gamma$  is an empirical transfer coefficient. We estimate  $\gamma$  by integrating and rearranging Equation 3:

$$\gamma = \dot{w}_b / (1 - r) e_*(T) \quad (4)$$

the overdot denoting a rate per unit time. We use the measured value of  $T$ , 296 K, and assume that  $r=0.80$ . For  $\dot{w}_b$  we adopt its average,  $7.86 \pm 0.40 \text{ mg min}^{-1}$ , over 33 measurements made during the course of this work, each with three replicate blank beakers. We assume standard errors of 0.05 for  $r$ , 0.25 K for  $T$ , and (consistent with the latter) 85 Pa for  $e_*$ . The result is an estimate of  $\gamma = 0.014 \pm 0.0036 \text{ mg min}^{-1} \text{ Pa}^{-1}$ .

Turning to the *additional* evaporative loss due to heating of the sample beaker,  $w_f$ , we have an expression analogous to Equation 3:

$$\begin{aligned} w_f &= \gamma \int_0^t [e_*(T + \delta T) - e_a] - [e_*(T) - e_a] dt' \\ &= \gamma \int_0^t [e_*(T + \delta T) - e_*(T)] dt' \\ &\equiv \gamma \int_0^t S \delta T dt' \end{aligned} \quad (5)$$

where  $\delta T$  is the temperature excess in the sample beaker and  $S = \partial e_*/\partial T$  may be evaluated at  $T + \frac{1}{2}\delta T$  using a standard expression. With  $\delta T$  known from measurements we can now estimate  $w_f$  by numerical integration. Based on our assumed standard error for temperature, we estimate a standard error of  $5 \text{ Pa K}^{-1}$  for  $S$ .

The heat released during digestion is roughly:

$$F_c \equiv -\Delta H M_c (w_t - w_b) \quad (6)$$

while the heat dissipated by excess evaporative cooling is:

$$\bar{F}_e = \lambda w_f \quad (7)$$

where  $\lambda = 2.45 \text{ J mg}^{-1}$  is the latent heat of vaporization. These two quantities are plotted in Figure 2b. The agreement is very good: about half of the heat of reaction appears to be dissipated by evaporative cooling, which is a very plausible result considering that we have ignored sensible heat loss to the insoluble sand, the beaker and the ambient air.

Equation 6 is based on Equation 2 with  $f=1$ . This is not accurate, because it does not contain the extra weight loss  $w_f$ , but it has the advantage of keeping  $F_c$  independent of  $F_e$ . The inaccuracy could be corrected easily by substituting  $w_b + w_f$  for  $w_b$ . In routine practice this would require measurements of  $\delta T$ , but in view of Figure 2b it seems reasonable to define and use a single correction factor  $f \neq 1$ . For each of our test measurements, we computed the quantity  $1 - w_f/(w_t - w_b)$ ; the average is  $f = 0.925 \pm 0.012$ , with 95 per cent confidence. Thus failure to correct for excess evaporation leads to estimates of carbonate abundance which are about 8 per cent too large.

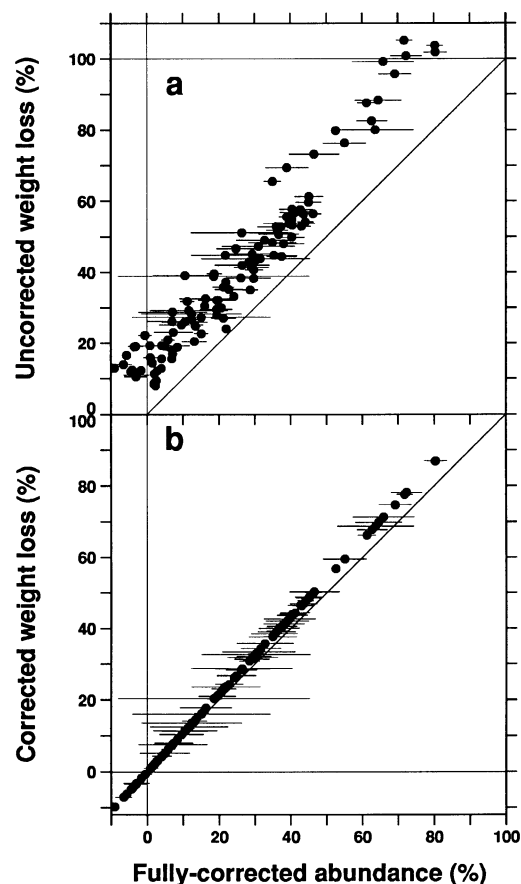


Figure 3. A comparison of fully corrected estimates of carbonate abundance against uncorrected and partly corrected estimates for each of 112 samples of till. The horizontal axis shows the best estimate of carbonate abundance (Equation 2). Error bars represent twice the standard error of each sample, based on three replicate measurements. (a) The vertical axis shows total proportional weight loss as an equivalent abundance of carbonate (i.e. Equation 2 with  $f=1$  and  $w_b=0$ ). (b) Evaporation-corrected weight loss as an equivalent abundance of carbonate, but without the correction for excess evaporation due to the heat of reaction (i.e. Equation 2 with  $f=1$ ).

Although this is a second-order correction, it costs nothing, rests on well-understood theory and, as shown above, can be verified experimentally with ease. Note that  $f$  corrects only for the thermodynamic enhancement of evaporation. There may be a kinetic enhancement as well, due to the bubbling which accompanies digestion.

## DISCUSSION

The losses  $w_t$  and  $w_b$  are measured independently, and  $w_b$  may vary in relative importance. In our particular set of measurements (Figure 3)  $M_c w_b / W_s$  ranged from 0.2 to 28 per cent. That is, evaporative weight loss alone, when expressed as an equivalent loss of calcite, reaches almost three-tenths of initial sample weight. It is, however, variable both relatively and absolutely, as the laboratory environment changes from one sample run to another.

The uncorrected weight loss  $M_c w_t / W_s$  ranges from 7 to 106 per cent (Figure 3a). That several samples have 'abundances' exceeding 100 per cent is a straightforward consequence of the bias due to neglect of evaporation.

The evaporation-corrected weight loss  $M_c (w_t - w_b) / W_s$  (Figure 3b) ranges from -11 to 87 per cent. With the final correction for the heat of reaction, our best estimates of carbonate abundance, plotted on the horizontal axis in Figure 3, range from -10 to 80 per cent (The negative values are discussed below.)

Omitting to correct for evaporation imposes a serious penalty in fidelity to nature. The bias in Figure 3a (i.e. the distance of each point above the diagonal line) is usually 10–20 per cent of equivalent carbonate abundance, and sometimes more. Correcting for the heat of reaction is necessary for single-digit accuracy, at least when abundances are large; in Figure 3b the corrected weight losses exhibit a constant bias of  $1/f$ , or about 8 per cent. In any substantial programme of measurements, some effort should probably be devoted to estimating  $f$  by procedures like those we have described, but a value near to our estimate of  $f=0.925$  may well be acceptable in smaller-scale investigations.

The corrections proposed above make simpler variants of the insoluble residue test viable as rapid, inexpensive and sufficiently accurate means for determining carbonate abundance. However, our results are not free of puzzling features. Several samples (e.g. Table I) yielded reproducible negative estimates of carbonate abundance, implying negligible dissolution and *reduced* evaporation in the sample beaker by comparison with the blank beaker. The anomalous samples were scattered across the study area, and were measured in different sample runs. We worked to usual standards of care in keeping glassware clean and we used reagent-grade HCl, so we do not think that laboratory cleanliness is at fault. The anomalous samples may have contained either an evaporation-retarding substance, such as a wax or resin, which collected as a film on the water surface, or an exotic solid which dissolved endothermically and thus consumed energy which would otherwise have been available for evaporation. We cannot rule out the presence of such a contaminant in other, more soluble samples. This problem, of which we have seen no mention in the literature, requires further investigation.

#### ACKNOWLEDGEMENTS

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